# Flow Behaviors of High Acyl Gellan Aqueous Solutions as Affected by Temperature, and Calcium and Gellan Concentrations

Yiqun Huang[*]         Pawan Singh Takhar[†]

Juming Tang[‡]         Barry G. Swanson[**]

[*]Queens College, the City University of New York, yiqun.huang@qc.cuny.edu

[†]Texas Tech University, pawan.takhar@ttu.edu

[‡]Washington State University, jtang@wsu.edu

[**]Washington State University, swansonb@wsu.edu

# Flow Behaviors of High Acyl Gellan Aqueous Solutions as Affected by Temperature, and Calcium and Gellan Concentrations[*]

Yiqun Huang, Pawan Singh Takhar, Juming Tang, and Barry G. Swanson

## Abstract

Rheological behaviors of high acyl (HA) gellan are not well understood partially because of its relatively late commercialization compared to low acyl gellan. The objective of this study was to investigate the effect of temperature (5-30 °C), calcium (0, 1 and 10 mM) and gellan concentrations (0.0044-0.1000% w/v) on the flow behaviors of high acyl gellan aqueous solutions using rheological tests. Gellan solutions with 0 or 1 mM added Ca++ exhibited shear thinning behavior at gellan concentrations above 0.0125%. The influence of temperature on apparent viscosity (shear rate, 100 s-1) of gellan solutions can be described with an Arrhenius relationship. The apparent viscosity of gellan solution at low concentrations was more sensitive to temperature changes. The addition of Ca++ led to a decrease in flow resistance for a dilute gellan solution (<0.0125%), but an increased resistance for a relatively concentrated gellan solution (>0.0125%).

KEYWORDS: gellan, high acyl, calcium, critical overlap concentration, viscosity

## 1. Introduction

Gellan gum is a food polysaccharide gelling agent produced through fermentation. It was approved by the US Food and Drug Administration for food use in 1992 (Kang, Veeder, Mirrasoul, Kaneko & Cottrell, 1982; Pszczola, 1993). Gellan polymer consists of tetrasaccharide (ABCD) repeating units, $\rightarrow$3)-$\beta$-D-Glcp-(1$\rightarrow$4)-$\beta$-D-GlcpA-(1$\rightarrow$4)-$\beta$-D-Glcp-(1$\rightarrow$4)-$\alpha$-L-Rhap (1$\rightarrow$) with the molar ratio of three monosaccharide residues (glucose (Glcp), glucuronic acid (GlcpA) and rhamnose (Rhap) as 2:1:1 (Jansson, Lindberg & Sandford, 1983). Two forms of commercially available gellan gum are high acyl (HA) and low acyl (LA) gellan. HA gellan contains acetate and glycerate groups at its glucose residues, while LA gellan does not. HA and LA gellan aqueous dispersion systems have vastly different rheological and functional properties (Tang, Tung & Zeng, 1997; Tang, Tung, Lelievre & Zeng, 1997; Mao, Tang & Swanson, 2000; Huang, Tang, Swanson & Rasco, 2003; Huang, Singh, Tang & Swanson, 2004).

Physicochemical properties of gellan aqueous solutions are affected by many factors, such as temperature, pH, gellan concentration, salts and sugars. HA gellan solutions generally have high apparent viscosities that are strongly dependent on cation concentrations (Sanderson, 1990). The study of Shimazaki and Ogino (1996) revealed a strong dependence of viscosity on the temperature and cations for LA gellan aqueous solutions. Jampen, Britt and Tung (2000) pointed out that the apparent viscosity ($\eta_{app}$) and the concentration (C, 0.5-2% w/w) of LA gellan (Kelcogel F) had a Power-law relationship, $\eta_{app} = 0.0151C^{1.77}$(45 °C, shear rate = 200 s$^{-1}$). The 0.5% LA gellan solutions were Newtonian at 45 °C or higher temperature, but non-Newtonian at a temperature lower than 45 °C, due to the partial gelation of the molecules.

Studies from various research groups indicate that gellan random coils in an aqueous environment can form double helices and further aggregate to a three-dimensional network at a very low gellan concentrations (Jampen et al., 2000; Rodríguez-Hernández, Durand, Garnier, Tecante & Joublier, 2003; Nickerson, Paulson & Speers 2003). The critical concentration (C*) is defined as the polymer concentration level above which an increase in polymer concentration results in a sharp increase in viscosity (Nickerson et al., 2003). The C* is considered as the maximum concentration of dilute solution behaviour, and is believed to be related to the formation of pre-gel or to be close to the gelation threshold (Jampen et al., 2000; Nickerson et al., 2003). The C* for LA gellan was reported to be 0.064% (w/v) (at 25ºC) by Jampen et al. (2000) and 0.0177% (w/w) (at 5 ºC and with 0.5 mM Na$^+$) by Nickerson et al. (2003), respectively. The C* of LA gellan solution decreases with an increase in cation concentrations or a decrease in temperature (Watase & Nishinari, 1993; Nickerson at al., 2003).

Rheological properties of gellan aqueous solutions were studied with several analytical methods over the past two decades. In particular, gellan solutions were characterized with a light scattering method (Takahashi, Akutu, Kubota & Nakamura, 1999), viscometry (Ogawa, 1999), NMR (Matsukawa, Tang & Watanabe, 1999) and rheometry (Takigawa, Nakajima & Masuda, 1999). Studies of gellan gum reported the effects of cations, sugars and pH on the physicochemical properties of gellan dispersions as well as the mechanisms of interactions of gellan gum with other gelling agents. However, most of these studies focused on LA gellan, while the basic properties of HA gellan are not as well studied in part due to its relatively late commercialization in 1998 (Morrison & Clark, 2000).

The objectives of this study were to investigate the basic flow behaviors of HA gellan aqueous solutions as affected by temperature, and calcium and gellan concentrations. Understanding the physicochemical properties of gellan aqueous solutions is essential for processing and quality control of liquid or semi-liquid food products containing gellan as thickening agent and/or stabilizer. Viscosity of a liquid or semi-liquid food product is closely tied to the product quality. It also affects the equipment design, heat transfer rate and pump performance during food processing operations (Nindo, Tang, Powers & Singh, 2005).

## 2. Materials and methods

### 2.1. Gellan solution preparation

Commercial HA gellan powder (Kelcogel LT100) used in the study was provided by CP Kelco US, Inc. (Wilmington, DE, USA). It had 92.3% solid, 5.8% ash, 0.0141% $Mg^{++}$, 0.321% $Ca^{++}$, 0.649% $Na^+$ and 2.029% $K^+$ on a wet weight basis (w/w, data were provided by CP Kelco). Gellan solutions ranging from 0.0044-0.1000% (w/v) with different levels of added calcium (0, 1mM, 10 mM) were prepared. The salt ($CaCl_2 \cdot 2H_2O$) used as $Ca^{++}$ additives was ACS reagent (Mallinckrodt Baker, Inc., Phillipsburg, NJ, USA). In preparing a gellan solution, a predetermined amount of gellan powder was dispersed into 200 ml of de-ionized water, or water containing 1mM $Ca^{++}$ or 10 mM $Ca^{++}$ in a 500 ml beaker. The solution was then heated to the boiling point with constantly stirring. Weight loss of the gellan solution during heating was recorded, and deionized water was added to compensate for the loss of water. The gellan solution was maintained at about 98 °C and stirred for two more min before used for rheological tests.

### 2.2. Rheological tests

Rheological tests were conducted with an AR2000 (TA Instruments, New Castle, Delaware, USA). A standard cup-and-bob geometry system with a conical end of the bob (DIN 12620) was used. The dimensions of the geometry system were as

follows: stator inner radius, 15.00 mm; rotor outer radius, 14.00 mm; cylinder immersed height, 42.00 mm; and gap 5.92 mm.

A series of steady state flow tests with the shear rate increasing from 1.452 to 1452 $s^{-1}$ were conducted at 20 °C. For a low-viscosity liquid, a high shear rate could lead to secondary flow effects and even the turbulent flow behavior, and thus increase flow resistance. For a fluid flowing in a Searle cylinder geometry system, its critical upper limit between laminar and turbulent flow behavior can be calculated using the Taylor number ($Ta$):

$$Ta = \frac{\omega_c \cdot \rho \cdot R_i^2 \cdot (\delta_{cc} - 1)^{3/2}}{\eta} \tag{1}$$

where $\omega_c$ is angular velocity, $\rho$ is solution density, $R_i$ is the radius of inner rotating bob, $R_o$ is the radius of the cup, and $\delta_{cc} = R_o/R_i$ (Mezger, 2002). The $Ta$ should be lower than 41.2 to maintain stable flow. Theoretically, **Eq. 1** applies only when $1 < \delta_{cc} < 1.04$. For the $\delta_{cc}$ value of 1.0714 used in this study, a more complicated equation should be used. However, the difference between the resulting shear rates by a more complex equation and by **Eq. 1** is within 5% for the $\delta_{cc}$ value of 1.0714 (Mezger, 2002). In this study, shear rates ranging from 1.452 to 231 $s^{-1}$ were used for data analysis of gellan solutions (except for 0.0044% gellan solution with 10 mM $Ca^{++}$). Since the apparent viscosity of the gellan solutions was greater than 1.7 mPas according to our experiments (**Fig. 1**), a shear rate less than 231 $s^{-1}$ would not cause flow instability according to the **Eq. 1**.

Apparent viscosity of a gellan solution (0.0063-0.1000% w/v) at a selected temperature (5, 10, 15, 20, 25, and 30 °C) was determined using peak hold step, in which a constant shear rate of 100 $s^{-1}$ was applied and the shear stress was recorded for a 2 min period.

### 2.3. *Characterization of flow behavior*
Rheology Advantage Data Analysis (V4.1.2, TA instrument, New Castle, Delaware, USA) was used to fit the flow curves of gellan solutions with functions including Power-law, Herschel-Bulkley, and Cross models. The Power-law model (**Eq. 2**) is normally used to describe shear-thinning or shear-thickening flow behavior without a yielding point, and is expressed as

$$\sigma = K\gamma^n \tag{2}$$

where $\sigma$ is shear stress, $\gamma$ is shear rate, $K$ is consistency index and $n$ is flow behavior index. The Herschel-Bulkley model (**Eq. 3**) is similar to the Power-law

model except that the yield stress ($\sigma_0$) is incorporated into the Herschel-Bulkley function,

$$\sigma = \sigma_0 + K\gamma^n \qquad (3)$$

Both Power-law and Herschel-Bulkley are used to describe flow behavior at medium shear rate range. The Cross model (**Eq. 4**) is normally applied for flow behavior consisting of high and low plateaus and shear-thinning behavior in-between over a wide range of shear rate (at least two decades) (Mezger, 2002). The Cross model is expressed as:

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + K\gamma^n} \qquad (4)$$

where $\eta$ is apparent viscosity, $\eta_0$ and $\eta_\infty$ are apparent viscosities at zero and infinite shear rates.

Standard error (SE, defined in **Eq. 5**) was used to evaluate the precision of an established flow model. The standard error (SE) was expressed as:

$$SE = \frac{\left( \sum_{i=1}^{n} (y_i - y_i')^2 \middle/ (n-2) \right)^{1/2}}{(y_n - y_1)} \times 1000 \qquad (5)$$

where $y_i$ is the measured value of shear stress, $y_i'$ is the shear stress value calculated by the model, and $n$ is the number of data points. A model with SE less than 20 was considered as reasonably fitting the flow curves (V4.1.2, TA instrument).

## 3. Results and discussion

### 3.1. Effect of gellan concentration on flow resistance

**Fig. 1** shows flow curves and viscosity curves for some representative gellan solutions ranging from 0.0063% to 0.1000% (w/v) at 20 °C. A linear relationship was observed between shear stress and shear rate when they were plotted in double logarithmic scales for all tested gellan solutions (**Fig. 1a**). The flow

curves of gellan solutions over the range from 0.0063% to 0.1000% were well modeled with Power-law function ($R^2$: 0.983 – 1.000, **Table 1**),

We observed a clear linear relationship between the flow behavior index (n) and gellan concentration, as well between logarithmic value of consistency index (K) and gellan concentration (**Fig. 2**). As the gellan concentration increased, the flow resistance and shear-thinning behavior of gellan solution enhanced, as indicated by an increase in the value of *K* and a decrease in the value of n (**Table 1**). Since the 0.0063% gellan solution has an *n* value close to 1, this gellan solution basically followed Newton's law and had an ideal viscous flow behavior. Shear-thinning behavior is commonly seen in carbohydrate polymer solutions (Jampen et al., 2000; Zhang, Zhou & Hui, 2005) that is generally explained with the entanglement model.

This model suggests that macromolecules exist as random coils that may entangle with each other at rest. The ratio of entangled and disentangled molecules is a constant (K) at equilibrium. Under a shear force, macromolecules

Table 1. Parameters and performance of Power-law models for HA gellan solutions (0.0063-0.1000% w/v) at 20 °C.

| Gellan (%) | $K$ (Pa s$^n$) | $n$ | Standard error | $R^{2*}$ |
|---|---|---|---|---|
| 0.0063 | 0.001951 | 1.015 | 2.276 | 0.9994 |
| 0.0125 | 0.002963 | 0.9801 | 1.493 | 0.9998 |
| 0.0188 | 0.005065 | 0.9190 | 2.416 | 0.9995 |
| 0.0250 | 0.007283 | 0.8900 | 1.973 | 0.9997 |
| 0.0313 | 0.01416 | 0.8054 | 3.094 | 0.9994 |
| 0.0375 | 0.0263 | 0.7292 | 5.062 | 0.9983 |
| 0.0500 | 0.1122 | 0.5557 | 3.495 | 0.9990 |
| 0.0625 | 0.2941 | 0.4592 | 6.962 | 0.9980 |
| 0.0750 | 0.6003 | 0.3766 | 10.55 | 0.9938 |
| 0.1000 | 4.101 | 0.1022 | 16.97 | 0.9831 |

$R^2$ of calculated values of shear stress vs. measured values of shear stress at logarithmic scales

are oriented into the shear direction, and therefore the amount of disentangled molecules is reduced (K decreases) to lower flow resistance, which leads to shear-thinning behavior (Mezger, 2002). As the polymer concentration increases, an enhanced shear-thinning behavior can be explained by the decrease in n value (Fig. 2).

Herschel-Bulkley models showed similar results as the Power-law models when fitting the flow curves of all tested solutions with gellan concentrations ranging from 0.0063-0.1000%. This indicated that there was no yield stress or the

value of yield stress was very small that can be neglected. The Cross model fitted slightly better for the flow curves of 0.0500-0.1000% gellan solutions than the Power-law model.
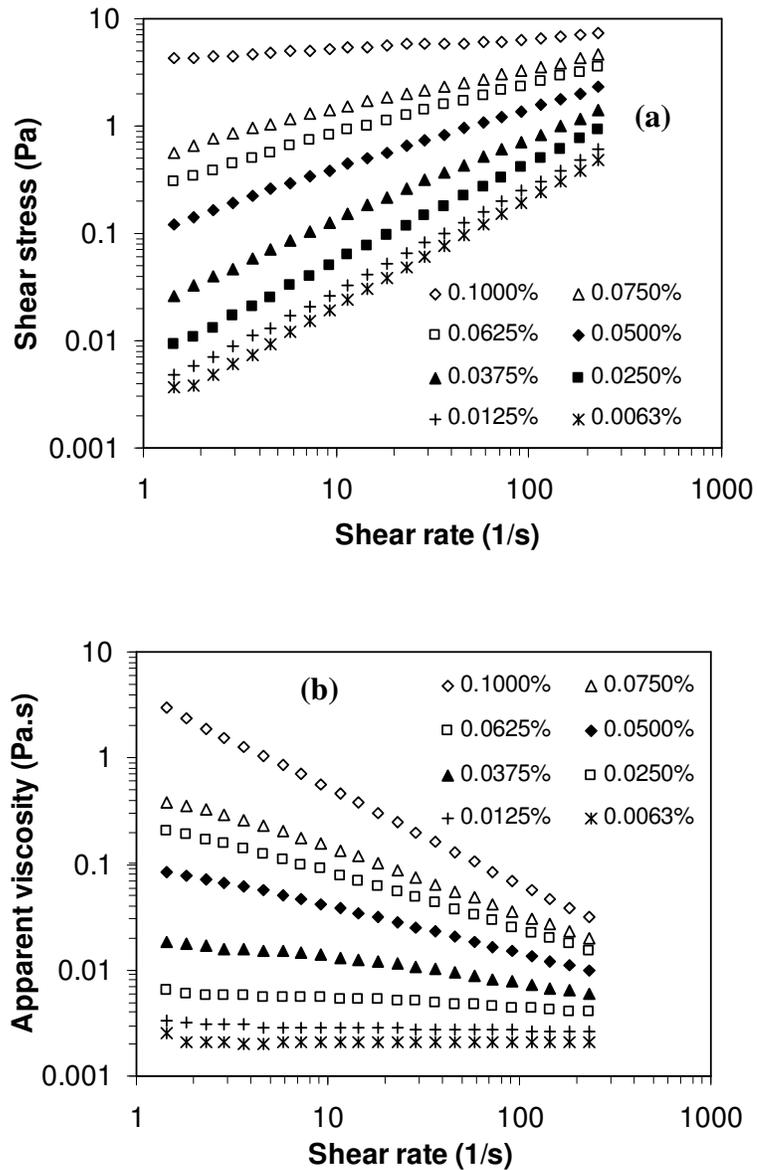


Fig. 1. (a) Flow curves, and (b) viscosity curves of gellan solutions (0.0063%-0.1000% w/v) at 20 °C.
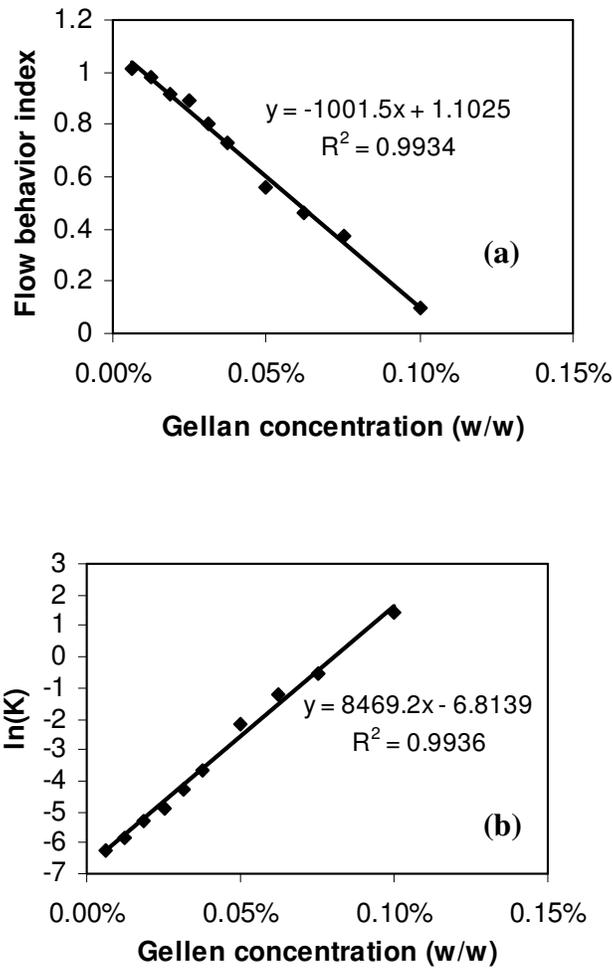
Fig. 2. (a) Gellan concentration vs. flow behavior index, and (b) gellan concentration vs. ln(k) at 20 °C.

The standard error of Cross models ranged from 1.26 to 4.21, compared to that of the Power-law models from 3.50 to 16.97 for 0.0500-0.1000% gellan solutions. Aggregation of gellan molecules may happen in a relatively concentrated gellan solution, which increases the complexity of the system, and thus Cross models may fit better than simpler models, such as Power-law model.

*3.2. Effects of temperature and gellan concentration on apparent viscosity at a constant shear rate*

The effect of temperature on the apparent viscosity ($\gamma$ =100 s$^{-1}$) of gellan solutions varies with gellan concentration. For 0.0063-0.0625% gellan solutions, an increase in temperature resulted in a decrease of apparent viscosity (**Fig. 3**). However, for 0.0750% and 0.1000% gellan solutions, as the temperature increased, the apparent viscosity increased first and then decreased, and a maximum apparent viscosity was observed at 20 °C (**Fig. 3b**).
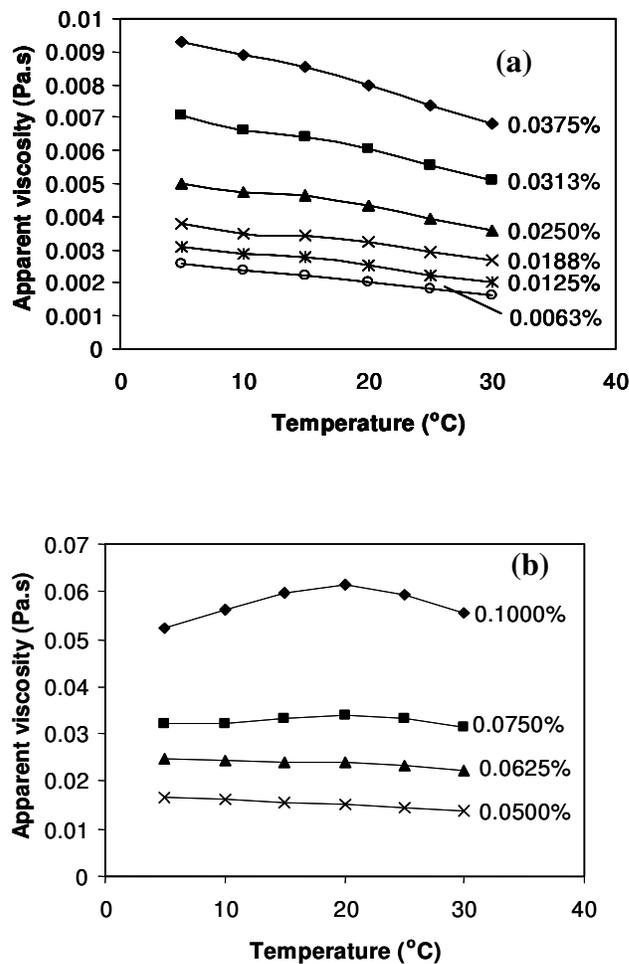


Fig. 3. Effects of temperature on apparent viscosity of solutions containing (a) 0.0063-0.0375%, and (b) 0.0500-0.1000% gellan at a shear rate of 100 s$^{-1}$.

A relatively high gellan concentration may cause partial gelation or pre-gel formation. This increases the complexity of the system that is difficult to be explained with simple apparent viscosity data at a constant shear rate in the study.

For 0.0063-0.0500% gellan solutions, the influence of temperature on the apparent viscosity ($\eta$) can be described with an Arrhenius relationship,

$$\eta = A \cdot \exp\left(\frac{E_a}{RT}\right), \qquad \gamma = 100 \text{ s}^{-1}, \qquad R^2 = 0.945\text{-}0.985 \qquad (6)$$

where $A$ is a constant, $E_a$ is activation energy (J/mol), $R$ is universal gas constant (8.314 J/mol·K), and $T$ is absolute temperature (K). The $E_a$ was calculated as 5.42 to 12.85 kJ/mol for gellan solutions ranging from 0.0063-0.0500% (**Table 2**).

Table 2. Parameters for Arrhenius relationship used to model the effects of temperature (5-30 °C) on apparent viscosity of HA gellan solutions (0.0063-0.0500% w/v)

| Gellan (%) | $E_a$ (kJ/mol) | A (mPa s) | $R^{2*}$ |
|-----------|-----------|-----------|-----------|
| 0.0063 | 12.85 | 0.010 | 0.9848 |
| 0.0125 | 11.72 | 0.020 | 0.9630 |
| 0.0188 | 9.37 | 0.067 | 0.9544 |
| 0.0250 | 9.28 | 0.093 | 0.9451 |
| 0.0313 | 8.74 | 0.163 | 0.9724 |
| 0.0375 | 8.73 | 0.218 | 0.9724 |
| 0.0500 | 5.42 | 1.610 | 0.9754 |

* $R^2$ of ln ($\eta$) vs. (1/RT) for Eq. 6

The $Ea$ increased as the gellan concentration decreased. Since a higher $Ea$ indicates that the change of solution temperature causes a more rapid change in viscosity (Steffe, 1996), the viscosity of a solution with lower gellan concentration was more sensitive to the change of temperature than that of the solutions with higher gellan concentration. At the same temperature, there was a linear relationship ($R^2 = 0.993\text{-}0.997$) between gellan concentration and ln($\eta$).

To incorporate the effect of gellan concentration on apparent viscosity into the **Eq. 6**, two equations (**Eq. 7** and **Eq. 8**) were tested to fit the experimental data using nonlinear regression with Matlab 7.2 (The MathWorks Inc., Natick, MA).

$$\eta = K \cdot \exp\left(\frac{E}{RT} + BC\right) \qquad (7)$$

$$\eta = K \cdot \exp\left(\frac{E}{RT}\right) C^{B} \tag{8}$$

where *C* is the gellan concentration in decimal, *K*, *E* and *B* are constants. For **Eq. 7**, data did not converge. All the parameters showed wild fluctuations, by slight variation in initial guess. However, **Eq. 8** fitted the data well, with a value of 0.965 for the $R^2$ of predicted *η* vs. experimental *η* . The values of *K*, *E* and *B* were calculated as 252.31, 6674.79, and 1.6483 for **Eq. 8**. Although these constants had no defined physical meaning, the **Eq. 8** can be used to predict the apparent viscosity ($\gamma =100$ s$^{-1}$) for HA gellean solution ranging from 0.0063% to 0.0500% at a temperature of 5-30 °C.

At a specific temperature, as the gellan concentration increased from 0.0188% to 0.0250%, there was a sudden increase in apparent viscosity (**Fig. 4**). Two linear regression functions (viscosity vs. gellan concentration at double logarithmic scale) were developed for 0.0063-0.0188% and 0.0250-0.1000% gellan solutions for each of the six tested temperature conditions. The C* was determined by calculating the overlapped point of two linear regression functions. The C* was in the range of 0.0219-0.0230% (or 0.0203-0.0213% for pure gellan if the water in the tested commercial gellan is considered) for gellan solution at temperature ranging from 5 to 30 °C. The C* increased as the temperature increased from 5 to 30 °C, although the effect of temperature on C* was not very obvious in the tested temperature range. To the best of our knowledge, there was no report on the C* of HA gellan solution. However, the C* for LA gellan was 0.064% (w/v) (at 25ºC) as reported by Jampen et al. (2000), and 0.0177% (w/w) (at 5 ºC and with 0.5 mM Na$^+$) by Nickerson et al. (2003), respectively. The C* of HA from this study was close to the C* of LA gellan as reported by Nickerson et al. (2003).

The C* is normally considered to be the maximum concentration of dilute solution behavior (Nickerson et al., 2003). In a simplified system, polymer molecules are believed to be completely isolated with no entanglement among molecules when the polymer concentration is lower than C*, and an increase in viscosity above C* was caused by the entanglement of macromolecules (Jampen at al., 2000; Nickerson et al., 2003).

We hypothesizes that gellan solutions are dynamic systems that involve both entanglement and disentanglement due to the thermodynamic movements of water and gellan molecules. In dilute solutions (<C*), the entanglements are transient. In semi-dilute solutions (>C*), some entanglement are relatively permanent due to the formation of hydrogen or other chemical bonds. The balance between transient and relatively permanent entanglements shifts with temperature, as reflected in the observed increase in C* with temperature. A rapid increase in

viscosity above C* can be explained as the result of an increase in the ratio (K value) of entangled and disentangled molecules.
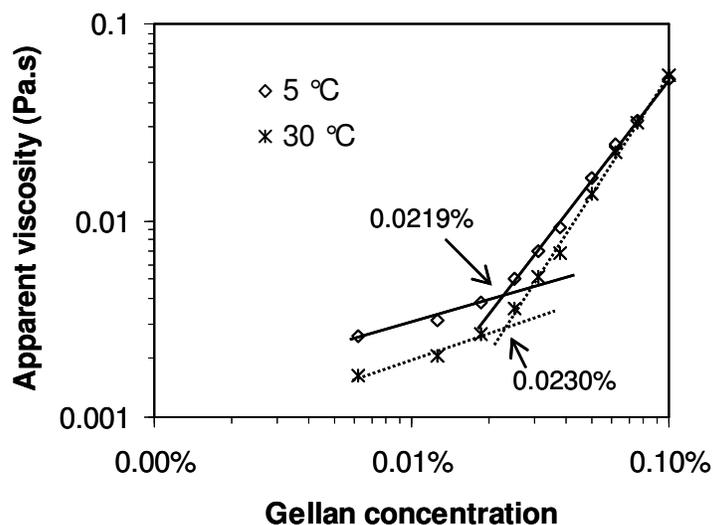


Fig 4. C* was calculated as the overlapped point of two linear regression functions (gellan concentration vs. apparent viscosity) for 0.0063-0.0188% and 0.0250-0.1000% gellan solutions, respectively (Shear rate = 100 s$^{-1}$). For 10-25 °C, the overlapped points were between 0.0219 to 0.0230%.

*3.3. Effects of calcium concentration*
Similar to the gellan solutions with no added Ca$^{++}$ (**Fig 1**), gellan solutions with 1 mM Ca$^{++}$ showed shear-thinning behavior, and the shear-thinning enhanced as the gellan concentration increased (**Fig. 5**). However, no similar trend was observed for gellan solutions containing 10 mM Ca$^{++}$, particularly for solutions containing more than 0.0250% gellan (**Fig. 6**).

The effect of Ca$^{++}$ on the flow resistance of gellan solution varies depending on the calcium and gellan concentration. Addition of 1mM or 10 mM Ca$^{++}$ caused an increased flow resistance for relatively concentrated gellan solutions containing 0.0188% or more gellan gum, and concentrated gellan solutions with 1 mM Ca$^{++}$ showed higher flow resistance than their 10 mM Ca$^{++}$ counterparts (**Fig. 7**). However, adding 1 mM or 10 mM Ca$^{++}$ in dilute gellan solution (such as 0.0063%) resulted in a reduced flow resistance; for intermediate solution (such as 0.0125% gellan), adding 1 mM Ca$^{++}$ led to an increased flow resistance, but adding 10 mM Ca$^{++}$ resulted in a reduced flow resistance (**Fig. 7**).
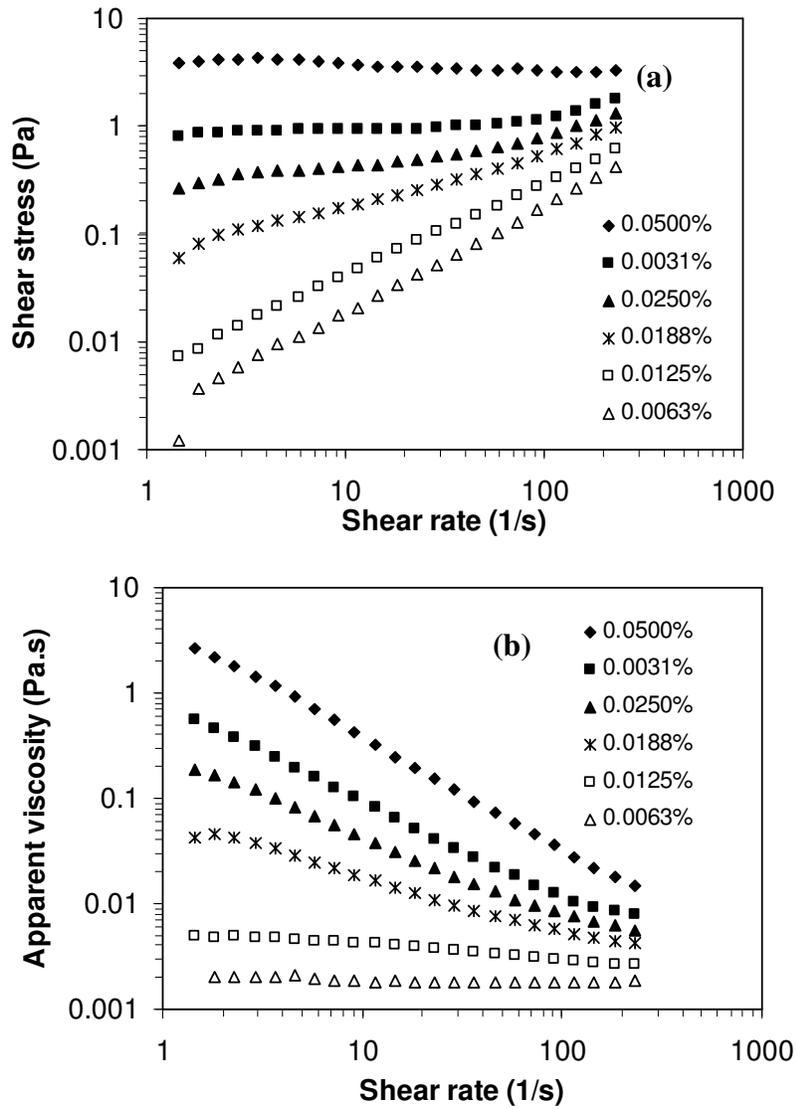
Fig. 5. (a) Flow curves, and (b) viscosity curves of gellan solutions (0.0063% - 0.0500% w/v) with 1 mM $Ca^{++}$ added at 20 °C.
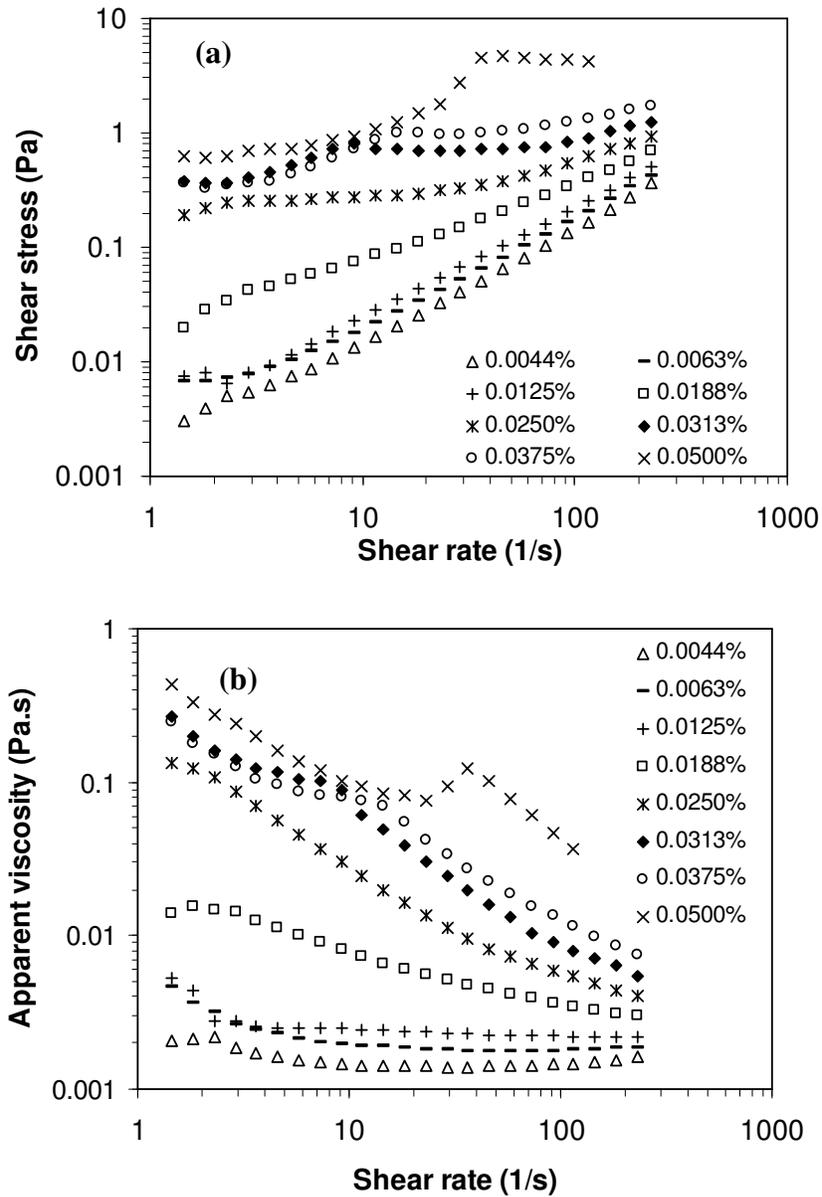
Fig. 6. (a) Flow curves, and (b) viscosity curves of gellan solutions (0.0044% - 0.0500% w/v) with 10 mM $Ca^{++}$ added at 20 °C.
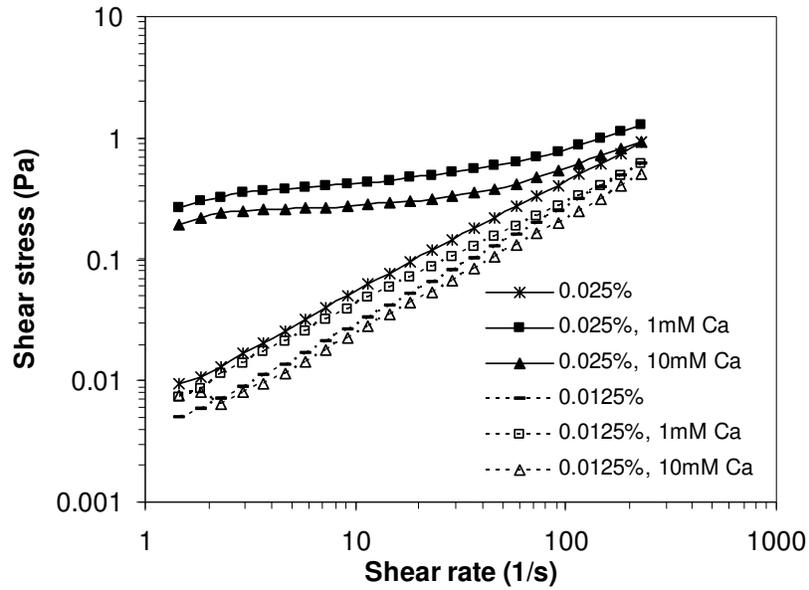
Fig. 7. Flow curves of representative gellan solutions with and without adding $Ca^{++}$ at 20 °C.
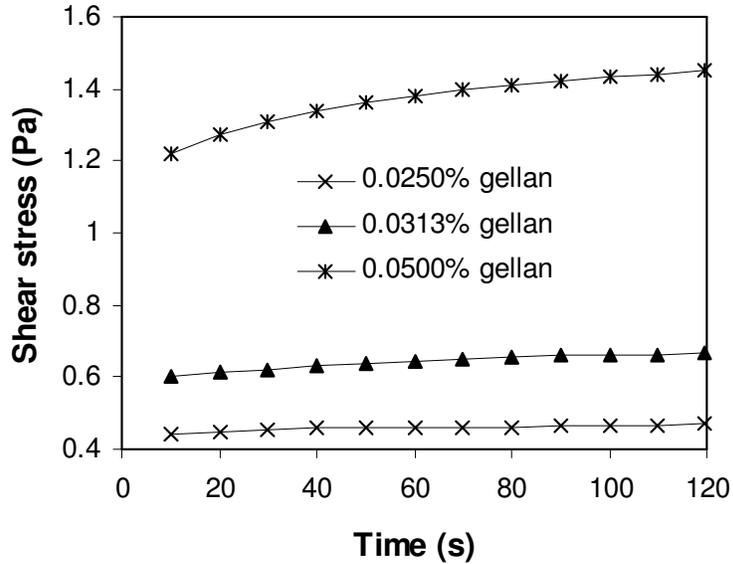


Fig. 8. Time dependent behavior of gellan solution with 1 mM $Ca^{++}$ at a constant shear rate of 100 $s^{-1}$ and 20 °C.

In a relatively concentrated gellan solutions ($\geq$ 0.0188%), calcium cations promote the helix formation and aggregation of macromolecules by forming ionic bonds with carboxylate groups of gellan molecule, and therefore increase gellan effective molecular weights and the flow resistance. In addition, the calcium cations affect the charge density of gellan macromolecules and change the electrostatic barrier to be less or more repulsive (Matsukawa et al., 1999). For a gellan solution, there may be an optimum $Ca^{++}$ concentration ($Ca^{++}$-opt) that provides enough cations to bind all the carboxyl group of gellan molecules, and also minimize the repulsive force among macromolecules. At $Ca^{++}$-opt, the system is least stable, and gellan molecules have the maximum ability to form gel or pro-gel. If the $Ca^{++}$ concentration is below the $Ca^{++}$-opt, $Ca^{++}$ promotes helix formation, while the repulsive effect caused by electrostatic barrier is less than this promotion effect, and thus an increase in $Ca^{++}$ would increase the association of macromolecules. On the other hand, if the $Ca^{++}$ is higher than the $Ca^{++}$-opt, it leads to an increased electrostatic barrier of gellan molecules, and therefore an increase in $Ca^{++}$ can stabilize the system by hindering the association of macromolecules, and the solution shows a reduced flow resistance. This assumed mechanism can explain that the effect of $Ca^{++}$ on flow resistance of gellan solutions varies depending on the gellan and $Ca^{++}$ concentration.

The effects of $Ca^{++}$ on flow resistance became less obvious as the shear rate increased for relatively concentrated gellan solution, such as 0.0250% gellan solution (**Fig. 7**). It is very likely that a weak gel structure forms at relatively concentrated gellan solution, but a high shearing force destroys the structure. The higher the shear rate, the more difficult for the system to regain its gel or pro-gel structure since formation of gel is time sensitive. **Fig. 8** showed that at a constant shear rate of 100 $s^{-1}$, an increase in shear stress with time was observed for solutions contains 0.025% or higher gellan concentration with 1 mM $Ca^{++}$. This indicated the formation of gel in these solutions and the gel formation is time sensitive (Mezger, 2002). No similar result was observed for other tested solutions except for 0.0100% gellan at a relative low temperature condition (5-15 °C). To study solutions involving gel or pro-gel formation, small deformation viscoelastic testing such as oscillatory testing (Huang et al. 2004) should be used.

## References

Huang, Y., Tang, J., Swanson, B. G., & Rasco, B. A. (2003). Effects of calcium concentration on textural properties of high and low acyl mixed gellan gels. *Carbohydrate Polymers*, 54, 517-522.

Huang, Y., Singh, P. P., Tang, J., & Swanson, B. G. (2004). Gelling temperature of high acyl gellan as affected by monovalent and divalent cations. *Carbohydrate Polymers*, 56, 27-33

Jampen, S., Britt, I. J., & Tung, M. A. (2000). Gellan polymer solution properties: dilute and concentrated regimes. *Food Research International*, 33, 579-586.

Jansson, P. E., Lindberg, B., & Sandford, P. (1983). Structural studies of gellan gum, an extracellular polysaccharide elaborated by Pseudomonas elodea. *Carbohydrate Research*, 124, 135-139.

Kang, K. S., Veeder, G. T., Mirrasoul, P. T., Kaneko, T., & Cottrell, I. W. (1982). Agar-like polysaccharide produced by a Pseudomonas species: production and basic properties. *Applied and Environmental Microbiology*, 43, 1086-1091.

Mao, R., Tang, J., & Swanson, B. G. (2000). Texture properties of high and low acyl mixed gellan gels. *Carbohydrate polymers*, 41, 331-338.

Matsukawa, S., Tang, Z., & Watanabe, T. (1999). Hydrogen-bonding behavior of gellan in solution during structural change observed by ^{1}H NMR and circular dichroism methods. *Progress in Colloid and Polymers Science,* 114, 15-24.

Mezger, T. G. (2002). The rheology handbook for users of rotational and oscillatory rheometers (pp. 32-33, 169-171). Hannover: Vincentz Verlag,

Morrison, N. A., & Clark, R. C. (2000). New textures with high acyl gellan gum. IFT Annual Meeting, Dallas, TX.

Nickerson, M. T., Paulson, A. T., & Speers, R. A. (2003). Rheological properties of gellan solutions: effect of calcium ions and temperature on pre-gel formation. *Food Hydrocolloids*, 17, 577-583.

Nindo, C. I., Tang, T., Powers, J. R., & Singh, P. (2005). Viscosity of blueberry and raspberry juices for processing applications. *Journal of Food Engineering*, 69, 343-350.

Ogawa, E. (1999). Temperature dependence of the conformational properties of sodium-type gellan gum in aqueous solutions. *Progress in Colloid and Polymers Science*, 114, 8-14.

Pszczola, D. E. (1993). Gellan gum wins IFT's food technology industrial achievement award. *Journal of Food Technology*, 47(9), 94-96.

Rodriguez-Hernandez, A. I., Durand, S., Garnier, C., Tecante, A. & Joublier. J. L. (2003). Rheology-structure properties of gellan systems: evidence of network formation at low gellan concentrations. *Food Hydrocolloids*, 17**,** 621-628.

Sanderson, G. R. (1990). Gellan gum. In P. Harris. Food Gels (pp. 201-232). London, England: Elsevier Science Publishers.

Shimazaki, T. & Ogino, K. (1996). Viscoelastic properties of $Ca^{2+}$- and $Na^{+}$- gellan gum aqueous solutions. *Carbohydrate Polymers*, 30, 95-100.

Steffe, J. F. (1996). Rheological methods in food process engineering (pp. 33-35). East Lansing, MI: Freeman Press.

Tang, J., Tung, M.A., Lelievre, J., & Zeng, Y. (1997). Stress-strain relationships for gellan gels in tension, compression and torsion. *Journal of Food Engineering*, 31, 511-529.

Tang, J., Tung, M. A., & Zeng, Y. (1997). Gelling properties of gellan solutions containing monovalent and divalent cations. *Journal of Food Science*, 62, 688-692,712.

Takigawa, T., Nakajima, K., & Masuda, T. (1999). Rheological properties of the gellan/water system. *Progress in Colloid and Polymers Science*, 114, 62-67.

Takahashi, R., Akutu, M., Kubota, K., & Nakamura, K. (1999). Characterization of gellan gum in aqueous NaCl solution. *Progress in Colloid and Polymers Science*, 114, 1-7.

Watase, M., & Nishinari, K. (1993). Effect of potassium on the rheological and thermal propertiesof gellan gum gels. *Food hydrocolloids*, 7, 449-456.

Zhang, L. M., Zhou, J. F., & Hui, P. S. (2005). Thickening, shear thinning and thixotropic behavior of a new polysaccharide-based polyampholyte in aqueous solutions. *Colloids and Surface A: Physicochemistry Engineering Aspects*, 259, 189-195.